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M. Berrondo, L. S. GarcíaColín, and J. RoblesDomínguez

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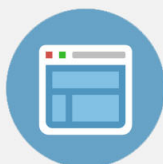
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The affinity in local chemical equilibrium *

M. Berrondo[†]

Instituto de Física, University of Mexico, Apdo. Postal 20-364, México 20, D.F., México

L. S. García-Colín[‡] and J. Robles-Domínguez

Departamento de Física y Química, UAM, Iztapalapa, Apdo. Postal 55-534, México 13, D.F., México

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We prove a generalized version of the H theorem for a Boltzmann-like equation which includes a reactive term for a bimolecular reaction. We find the hydrodynamic equations for the reactive system as well as the distribution function assuming local chemical equilibrium. The resulting chemical affinity vanishes identically as a consequence of the constraints imposed by the reaction. Finally we derive Gibbs relation for the local entropy production in terms of the chemical components, with the result that there appears no term in the affinity.

I. INTRODUCTION

The microscopic foundations of chemical reactions is mostly based on the use of Boltzmann's equation, generalized in such a way as to include reactive collisions. The homogeneous case has been studied in detail for bimolecular reactions,¹ deriving the rate equation, including expressions for the rate constants in terms of the reactive cross sections, following the pioneering works of Prigogine *et al.*² and Eliason and Hirschfelder.³ More recently, attention has been paid⁴ to the hydrodynamic equations in the reactive case, in order to include spatial inhomogeneities in the system, and the combined effects, which can hardly be overestimated. From this study,⁴ the need to look at the chemical reaction as a constraint has become evident. This, of course, is a common point of view in elementary chemistry textbooks. We can interpret this as due to the fact that, from all possible combinations of pairs of colliding molecule, only two of them (A, B and C, D) are reactive in a bimolecular reaction such as



This indeed imposes a constraint.

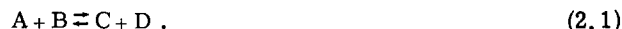
In this paper we shall concentrate on a system in local chemical equilibrium. By this we mean a system which is close to both thermal and chemical equilibrium. This in turn implies that the species densities depend on the equilibrium constants for the reaction, although we must give a local description in space and time. This is the case when the reactive collisions are frequent enough as to contribute in driving the system to equilibrium, and thus that the activation energies for the reaction to occur are very small as compared to the temperature. In a sense, it is the opposite case to the one considered in Refs. 1-3, where it is assumed that the local thermal equilibrium is attained in a time scale which is much shorter than the mean free time between reactive collisions. The intermediate regime is a case which certainly deserves further study.

Our starting point is again a kinetic equation including only binary collisions from which an H theorem is derived in Sec. II for this reactive case. In Sec. III we derive the conservation equations for the macroscopic quantities, taking into account the constraint im-

posed by the chemical reaction. The specific form of the local equilibrium distribution function is found in the case of interest, i. e., local chemical equilibrium. We proceed to define a chemical affinity in this case, which turns out to vanish identically. Section IV includes an expression for the entropy production in the local equilibrium case, and a brief comparison with the more familiar nonreactive expressions.

II. KINETIC EQUATION FOR A REACTIVE SYSTEM

We shall restrict our attention to a system in which a bimolecular reaction takes place, and assume it of the general form:



Since there are four different chemical species, the distribution function f must be labeled by a species index i ($i=1, 2, 3, 4$ for A, B, C, D). It must also specify the internal energy state, characterized by the internal quantum number α , as well as the center of mass position \mathbf{r}_i and velocity \mathbf{v}_i :

$$f_i \equiv f_i(\alpha, \mathbf{r}_i, \mathbf{v}_i, t). \quad (2.2)$$

The general form of the kinetic equation obeyed by this distribution function is^{1,2,4}:

$$\frac{\partial f_i}{\partial t} + \mathbf{v}_i \cdot \nabla f_i = J_{\text{col}}^{(\text{el})} + J_{\text{col}}^{(\text{in})} + J_{\text{col}}^{(\text{react})}, \quad (2.3)$$

where the collision terms must include elastic, inelastic, and reactive terms. In the low concentration limit, these are Boltzmann-like, i. e., include only binary collisions. The expressions are summed over all allowed collisions: the elastic and inelastic contributions:

$$J^{(\text{el})} = \sum_{j\beta} \int g_{ij} \sigma_{ij}(\alpha\beta, \alpha\beta; g_{ij}, \Omega) \times [f_i(\alpha, \mathbf{r}, \mathbf{v}'_i, t) f_j(\beta, \mathbf{r}, \mathbf{v}'_j, t) - f_i(\alpha, \mathbf{r}, \mathbf{v}_i, t) f_j(\beta, \mathbf{r}, \mathbf{v}_j, t)] d\mathbf{v}_j d\Omega \quad (2.4a)$$

$$J^{(\text{in})} = \sum_{j\beta\gamma\delta} \int g_{ij} \sigma_{ij}(\gamma\delta, \alpha\beta; g_{ij}, \Omega) \times [f_i(\gamma, \mathbf{r}, \mathbf{v}'_i, t) f_j(\delta, \mathbf{r}, \mathbf{v}'_j, t) - f_i(\alpha, \mathbf{r}, \mathbf{v}_i, t) f_j(\beta, \mathbf{r}, \mathbf{v}_j, t)] d\mathbf{v}_j d\Omega, \quad (2.4b)$$

and the reactive term, which is written explicitly for the case $i=1$:

$$J^{(\text{react})} = \sum_{\beta\gamma\delta} \int g_{AB} \sigma_{CD-AB}^R(\gamma\delta, \alpha\beta; g_{AB}, \Omega) \times [f_C(\gamma, \mathbf{r}, \mathbf{v}'_C, t) f_D(\delta, \mathbf{r}, \mathbf{v}'_D, t) - f_A(\alpha, \mathbf{r}, \mathbf{v}_A, t) f_B(\beta, \mathbf{r}, \mathbf{v}_B, t)] d\mathbf{v}_B d\Omega, \quad (2.4c)$$

with obvious changes for $i=2, 3, 4$. Here g_{ij} is the relative velocity in the collision between i and j , while σ refers to the cross section, and in particular σ^R to the reactive cross section. The constraint imposed by the reaction reflects in the fact that there is no summation over the species in the reactive term (2.4c).

Let us now prove the validity of an extended H theorem for this case, starting with the modified Boltzmann equation (2.3), (2.4). If we define the H function in the usual way:

$$H = \sum_{i,\alpha} \int f_i \ln f_i d\mathbf{r}_i d\mathbf{p}_i, \quad (2.5)$$

the total time derivative of H is obtained from (2.3). It involves the drift term plus the collision term, but the first one vanishes, as in the ordinary case.⁵ Using now the invariance of the product $g_{ij}\sigma_{ij}$ under the exchange $i \leftrightarrow j$ in each term, the contribution from the collision is finally expressed as a summation over i and j of terms like

$$\sum_{\substack{\text{int. quant.} \\ \text{numb.}}} \frac{1}{2} \int g_{ij} \sigma_{ij} (f'_i f'_j - f_i f_j) (2 + \ln f_i f_j) d\mathbf{r}_i d\mathbf{p}_i d\mathbf{p}_j d\Omega, \quad (2.6)$$

including the three different contributions from (2.4), with their respective limitations on the values of j and the internal quantum numbers.

The H theorem is now a direct consequence of the microscopic reversibility

$$g'_{ij} \sigma'_{ij} = g_{ij} \sigma_{ij}, \quad (2.7)$$

which is discussed in Ref. 1 in detail, including the reactive case. Equation (2.7) results from the unitarity of the S matrix⁶ in case there are no real bound states for the system $A-B$, which we shall assume in this paper.

Substituting (2.7) into (2.6), the H theorem follows in the same fashion as in the nonreactive case,⁷ by interchanging \mathbf{p} and \mathbf{p}' , and using (2.7), with the net result:

$$\sum_{ij} \sum_{\substack{\text{int. quant.} \\ \text{numb.}}} \frac{1}{4} \int g_{ij} \sigma_{ij} (f'_i f'_j - f_i f_j) \times \ln \left(\frac{f'_i f'_j}{f_i f_j} \right) d\mathbf{r}_i d\mathbf{p}_i d\mathbf{p}_j d\Omega \leq 0. \quad (2.8)$$

The equality holds if and only if the distribution function appearing in (2.8) represents local equilibrium,⁷ which implies that

$$f_i^{(0)'} f_j^{(0)'} = f_i^{(0)} f_j^{(0)} \quad (2.9)$$

for every couple (i, j) . Hence, for the local equilibrium distribution function

$$\frac{dH^{(0)}}{dt} = 0 \quad (2.10)$$

results as a straightforward extension of the nonreactive case.

III. HYDRODYNAMIC EQUATIONS

The macroscopic description can be given, in the reactive case, in terms of the numerical densities for each species, defined as:

$$n_i(\mathbf{r}, t) = \sum_{\alpha} \int f_i(\alpha, \mathbf{r}, \mathbf{v}_i, t) d\mathbf{v}_i \quad (3.1)$$

which, summed over i , yields the total numerical density $n = \sum_i n_i$. The mass density, using (3.1) is

$$\rho(\mathbf{r}, t) = \sum_i m_i n_i(\mathbf{r}, t), \quad (3.2)$$

where m_i is the mass of a molecule of species i .

In addition to these, let us define the chemical *components* and their numerical densities, following Andersen.⁴ The chemical species are not independent from each other since the Reaction (2.1) imposes a constraint on the way the species can change: Each time a molecule A disappears, there must appear a molecule C , and so on. For the bimolecular case (2.1), there are only three independent components which we shall label by J ($J=I, II, III$). These are defined in such a way that any of the four species A_i ($i=1, \dots, 4$) is expressed as a linear combination of the three components, and taking into account (2.1) for each collision: $A_1 + A_2 = A_3 + A_4$.

The definition of the components is not unique indeed, and we shall take a particular choice,⁴ namely

$$A_i = \sum_{J=I}^{III} N_{iJ} J \quad (3.3)$$

where the 4×3 matrix N is:

$$N = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \\ 1 & 1 & -1 \end{pmatrix}. \quad (3.4)$$

From this we can immediately define the component densities as

$$n_J(\mathbf{r}, t) = \sum_i N_{Ji} n_i(\mathbf{r}, t). \quad (3.5)$$

Written explicitly, they take the form

$$\begin{aligned} n_I &= n_1 + n_4, \\ n_{II} &= n_2 + n_4, \\ n_{III} &= n_3 - n_4, \end{aligned} \quad (3.5')$$

so that $\sum_J n_J = n$. In this way, we can work with the *component* densities without worrying any longer about the constraint imposed by the reaction. It is evident however that the information about the chemical reaction will only appear explicitly in the equations for the *species*' densities n_i .

The average local velocity \mathbf{u} and the local energy density U are given by the usual expressions

$$\rho \mathbf{u}(\mathbf{r}, t) = \sum_{i\alpha} m_i \int \mathbf{v}_i f_i d\mathbf{v}_i, \quad (3.6)$$

$$\rho U(\mathbf{r}, t) = \sum_{i\alpha} \int \left[\frac{1}{2} m_i V_i^2 + \epsilon_{i\alpha} \right] f_i d\mathbf{v}_i, \quad (3.7)$$

respectively, where $\epsilon_{i\alpha}$ is the internal energy of a molecule of species i in the internal state α , and we have introduced the peculiar velocity \mathbf{V}_i , measured with respect to the barycentric velocity

$$\mathbf{V}_i = \mathbf{v}_i - \mathbf{u}(\mathbf{r}, t). \quad (3.8)$$

In order to obtain the continuity equations for the densities defined above, we multiply the kinetic equation (2.3) by the appropriate quantity $\psi(i, \alpha, \mathbf{V}_i)$ and average by integrating over \mathbf{v}_i , summing over i and α . In case ψ is a collisional invariant, the weighted average stemming from the collision terms J_{col} in the kinetic equation (2.3) vanishes, so we obtain the conservation equations⁴ corresponding to

$$\begin{aligned} \psi &= m_i, \quad N_{iJ} \text{ (for each } J), \quad m_i V_i, \\ E_{i\alpha} &(\equiv \frac{1}{2} m_i V_i^2 + \epsilon_{i\alpha}), \end{aligned} \quad (3.9)$$

namely

$$\begin{aligned} \frac{D\rho}{Dt} + \rho \nabla \cdot \mathbf{u} &= 0, \\ \frac{Dn_J}{Dt} + n_J \nabla \cdot \mathbf{u} + \nabla \cdot \mathcal{J}_J &= 0, \\ \rho \frac{D\mathbf{u}}{Dt} + \nabla \cdot \vec{P} &= 0, \\ \rho \frac{DU}{Dt} + \nabla \cdot \mathcal{J}_q + \vec{P} : \nabla \mathbf{u} &= 0, \end{aligned} \quad (3.10)$$

where $D/Dt = \partial/\partial t + \mathbf{u} \cdot \nabla$ is the streaming derivative. In Eqs. (3.10) we introduced the "diffusion" numerical flux \mathcal{J}_J for component J

$$\mathcal{J}_J(\mathbf{r}, t) = \sum_i N_{Ji} \sum_{\alpha} \int \mathbf{V}_i(\mathbf{r}, t) f_i d\mathbf{v}_i, \quad (3.11)$$

the pressure tensor \vec{P} having the usual definition

$$\vec{P}(\mathbf{r}, t) = \sum_{i\alpha} m_i \int \mathbf{V}_i \mathbf{V}_i f_i d\mathbf{v}_i, \quad (3.12)$$

as well as the heat flux \mathcal{J}_q associated to the energy $E_{i\alpha}$ defined in (3.9)

$$\mathcal{J}_q = \sum_{i\alpha} \int E_{i\alpha} \mathbf{V}_i f_i d\mathbf{v}_i. \quad (3.13)$$

The densities which have a direct physical interpretation are of course the species densities n_i . The conservation equation for these follow by setting $\psi \equiv \delta_{ij}$. During a reactive collision, the species label necessarily changes, so δ_{ij} is *not* a collisional invariant. Hence there appears a contribution from the reactive term (2.4c). The resulting equation is the chemical reaction rate equation for inhomogeneous media,⁴ containing both diffusive and reactive terms

$$\frac{Dn_i}{Dt} + n_i \nabla \cdot \mathbf{u} + \nabla \cdot \mathcal{J}_i = K_i^{(\text{react})}. \quad (3.14)$$

The diffusion flux for species i is:

$$\mathcal{J}_i(\mathbf{r}, t) = \sum_{\alpha} \int \mathbf{V}_i f_i d\mathbf{v}_i, \quad (3.15)$$

and the reactive source term is given in terms of (2.4c) as

$$K_i^{(\text{react})} = \sum_{\alpha} \int J^{(\text{react})}(i, \alpha, \mathbf{v}_i) d\mathbf{v}_i. \quad (3.16)$$

In order to apply the Chapman-Enskog method in our case, we must distinguish between the two extreme cases: almost frozen flow (AFF) and local chemical equilibrium (LCE). In the AFF regime, the reactive collisions are considered to be much slower than the elastic and inelastic terms, so they do not change the equilibrium established (locally) by the nonreactive collisions in any appreciable way. In other words, the reactive term (2.4c) is considered as of zeroth order in the uniformity expansion parameter $\mu \sim (\text{mean free time})/(\text{macroscopic time})$. This regime has been discussed in detail by Ross *et al.*¹ for the homogeneous case, and also by Andersen⁴ in the inhomogeneous case. The reactive term (3.16) for AFF is evaluated explicitly by substituting the local equilibrium distribution constructed assuming that $\psi = \delta_{ij}$ is a collisional invariant. This is indeed consistent with the assumption that reactive collisions take no part in driving the system towards equilibrium. The chemical reactions in this case have a characteristic time so large that the system is allowed to relax equilibrium at each point in this time scale.

In the other regime (LCE), both chemical reactions and intermolecular relaxations are fast enough to alter the local distribution function. In this event, we must take the reactive collisions on the same footing as the elastic ones. The first order terms in μ yield the local (both thermal and chemical) equilibrium equations,⁴ when we use the expansion

$$f_i = f_i^{(0)} [1 + \mu \Phi^{(1)} + O(\mu^2)] \quad (3.17)$$

in the conservation equations.

In order to obtain the local equilibrium distribution function $f_i^{(0)}$, we use the H theorem derived in the last section to get that

$$J(f_i^{(0)}, f_j^{(0)}) = 0. \quad (3.18)$$

As usual, $\ln f^{(0)}$ has to be a linear combination of collisional invariants. For LCE we include N_{iJ} , rather than δ_{ij} , since (3.18) is also valid for reactive collisions. Assuming we have the same local temperature for all species, the equilibrium distribution function is expressed in terms of the invariants (3.9) as

$$f_i^{(0)}(\alpha, \mathbf{r}, \mathbf{v}_i, t) = \exp \left[-\beta \left(E_{i\alpha} - \sum_{J=I}^{\text{III}} N_{iJ} \alpha_J \right) \right]. \quad (3.19)$$

In (3.19), the total energy $E_{i\alpha}$ is given in terms of the peculiar velocity, as defined in (3.9). The temperature $kT = \beta^{-1}$ is defined as the average energy as usual:

$$\frac{3}{2} n(\mathbf{r}, t) kT(\mathbf{r}, t) = \sum_{i\alpha} \int E_{i\alpha}(\mathbf{r}, t) f_i^{(0)} d\mathbf{v}_i . \quad (3.20)$$

Finally, the parameters $\alpha_J(\mathbf{r}, t)$ play the role of "chemical potentials" for the components (notice that the α 's are defined with respect to the numbers N_{iJ} rather than the masses, since m_J has no meaning) $J = I, II, III$. With the definition of the species' numerical densities (3.1) we can write

$$n_i^{(0)}(\mathbf{r}, t) = \left(\frac{2\pi kT}{m_i} \right)^{3/2} Q_i \exp\left(\sum_J N_{iJ} \alpha_J \right) , \quad (3.21)$$

where $Q_i = \sum_{\alpha} \exp(-\epsilon_{i\alpha}/kT)$ is the internal partition function for molecule i .

For the particular choice (3.4) which defines the components, we can express α_J ($J = I, II, III$) in terms of the first three species densities $n_1^{(0)}, n_2^{(0)}, n_3^{(0)}$ as:

$$\alpha_{I,II,III}(\mathbf{r}, t) = kT(\mathbf{r}, t) \left(\ln \frac{n_{1,2,3}^{(0)}(\mathbf{r}, t)}{Q_{1,2,3}} - \frac{3}{2} \ln \frac{2\pi kT(\mathbf{r}, t)}{m_{1,2,3}} \right) . \quad (3.22)$$

In this way, we can identify them as the chemical potentials associated to the species densities

$$\alpha_{I,II,III} = \alpha_{1,2,3} . \quad (3.23)$$

Using (3.21) for $i = 4$, we can also define

$$\alpha_4 = \alpha_1 + \alpha_2 - \alpha_3 . \quad (3.24)$$

In other words, the chemical affinity in LCE is:

$$\alpha(\mathbf{r}, t) \equiv 0 . \quad (3.25)$$

IV. CHEMICAL AFFINITY AND GIBBS RELATION IN LCE

The way we identify components' chemical potentials with species' chemical potentials (3.23) is only valid for the particular choice of components (3.4). In LCE there are only three independent chemical potentials, each associated with each of the three components. This, of course is only a consequence of the constraint imposed by the reaction. Hence, if we insist on defining a chemical potential for each species, there must be a relation among them. This relation, Eq. (3.24) is independent of the choice made in (3.4) for the identification (3.23). Since the fact that the affinity is zero follows directly from (3.24), it will also be independent of the choice made to define the components. This is not so surprising as it might seem at first sight, since the chemical affinity is identically zero in chemical equilibrium, and it should be the same in LCE.

The perturbation Φ in the distribution function (3.17) has to fulfill in this case the restriction:

$$\sum_i N_{ji} \int f_i^{(0)} \Phi_i d\mathbf{v}_i = 0 \quad \forall J = I, II, III \quad (4.1)$$

to every order in μ . However there is no similar condition related to the species density (with N_{ji} replaced by δ_{ij}), as one has for AFF. Now, since we have constructed $f_i^{(0)}$ using (3.18) also for the reactive term, the RHS in the rate equation (3.14) vanishes to zeroth order in μ . To first order however, we get

$$\frac{Dn_i^{(1)}}{Dt} + n_i^{(0)} \nabla \cdot \mathbf{u}^{(1)} + \nabla \cdot \mathcal{J}_i^{(1)} = K_i^{(1)} \neq 0 , \quad (4.2)$$

where

$$n_i^{(1)} = \sum_{\alpha} \int f_i^{(0)} (1 + \Phi_i^{(1)}) d\mathbf{v}_i \equiv n_i^{(0)} + \delta n_i . \quad (4.3)$$

In spite of the fact that the reaction source term vanishes to order zero in μ , there is a first order contribution $K_i^{(1)}$ which does not vanish any longer. It is instead linear in $\Phi_i^{(1)}$ when we substitute (3.17) in the expression (3.16). The net result is hence a linearized chemical rate equation in terms of δn_i , for the case of LCE.

The important result (4.2) means that the chemical reaction takes place away from (absolute) chemical equilibrium, in spite of the fact that the chemical affinity vanishes.

Let us next look at the expression for the local entropy density at equilibrium:

$$\rho s = -k \sum_{i\alpha} \int f_i (\ln f_i - 1) d\mathbf{v}_i , \quad (4.4)$$

which, using (3.19), (3.1), and (3.7) results in

$$\rho s = \frac{1}{T} \left(p + \rho U - \sum_{J=I}^{III} \alpha_J n_J \right) , \quad (4.5)$$

where p is, as usual, the hydrostatic pressure. In order to obtain Gibbs relation we differentiate (4.5) with respect to time, and use the conservation equations (3.10). The final result differs from the AFF case⁸ in the fact that all the summations which appear are made over components rather than species, and there is no contribution coming from the reactive source term—since the affinity vanishes

$$\rho \frac{Ds}{Dt} = -\nabla \cdot \mathcal{J}_s - \frac{1}{T^2} \mathcal{J}_q \cdot \nabla T - \sum_J \mathcal{J}_J \cdot \nabla \left(\frac{\alpha_J}{T} \right) - \frac{1}{T} \bar{\Pi} : \nabla \mathbf{u} , \quad (4.6)$$

where

$$\bar{\Pi} \equiv \bar{P} - pI ,$$

and

$$\mathcal{J}_s \equiv \frac{1}{T} \mathcal{J}_q - \sum_J \alpha_J \mathcal{J}_J . \quad (4.7)$$

The corresponding expression for the entropy production is

$$\sigma = \mathcal{J}_q \cdot \nabla \left(\frac{1}{T} \right) + \sum_J \mathcal{J}_J \cdot \nabla \left(-\frac{\alpha_J}{T} \right) - \frac{1}{T} \bar{\Pi} : \nabla \mathbf{u} . \quad (4.8)$$

Here we see that for LCE the most natural fluxes to consider are the fluxes \mathcal{J}_J associated to the numerical densities of the components, together with their chemical potentials α_J . In fact, Expressions (4.6) and (4.8) look formally like those of a nonreactive multicomponent system,⁸ with the components replacing the species. In other words, the effect of the chemical reaction is not apparent in the entropy production because the zeroth order reactive term in the μ expansion vanishes.

V. CONCLUSIONS

In this paper we have found that in LCE the chemical affinity vanishes identically. Nevertheless the reactive

source term in the rate equation is not zero, so this is not equivalent to absolute chemical equilibrium. LCE implies only that the zeroth order (in μ) reactive contribution vanishes. The first order reaction term is linear in δn_i , hence yielding a linearized version of the chemical rate equation (3.14), which is characteristic of local equilibrium. Notice that it is not enough to assume local thermal equilibrium (this is also the case in AFF), but also LCE in order to obtain a linear rate equation for this nonhomogeneous case. The first order contribution does appear in the entropy production, which takes an orthodox form, as long as we express it in terms of the independent chemical components. Since the measurable quantities are the chemical species, this implies a cumbersome entanglement of the diffusive effects with reactive ones, as well as the crossed effects due to the thermal fluxes. It is not at all clear how these effects can be separated in the case of LCE.

We would also like to point out the difference between the affinity and the barycentric velocity in this case. In equilibrium u takes the value zero, since we are assuming there are no external forces. The affinity instead vanishes identically in chemical equilibrium, therefore it has to be the same (zero) in LCE.

In the particular case of a homogeneous system there are no divergence terms in the rate equation (3.14), which reduces to:

$$dn_j(t)/dt = 0 \quad (5.1)$$

For the particular choice (3.4), this implies conservation of $n_1 + n_4$, $n_2 + n_4$, and $n_3 - n_4$, so we can introduce the progress variable $\xi(t)$ in the familiar fashion,⁸ in spite of the fact that the affinity vanishes.

Finally, we expect the main conclusions in this paper to remain valid if we include higher order terms in the density, since they are based on the hydrodynamic equations. The specific form of the reactive source term in the rate equations (3.14) and (4.2) will indeed change, but not so the entropy production, neither the vanishing of the affinity in local chemical equilibrium.

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†Consultant at Instituto Mexicano del Petróleo, México.

††Also at Facultad de Ciencias, UNAM, México 20, D. F.

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